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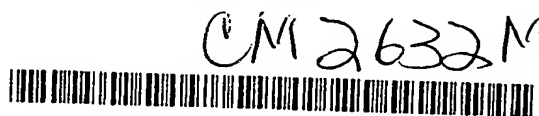
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(71) Applicant (for all designated States except US): **THE PROCTER & GAMBLE COMPANY** [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **BOSWELL, Henry, Drummond** [GB/GB], Flat 2, 6 Sidney Road, Guildford, Surrey GU1 3LJ (GB) **MARSH, Jennifer, Mary** [GB/GB]; 29 King James Way, Henley-On-Thames, Oxfordshire RG9 1XL (GB) **OLSHAVSKY, Michael, Andrew** [US/US]; 9070 Saddlewood Place, Mason, OH 45040 (US) **PARK, John, Scott** [GB/GB], 55 Springfield Avenue, Aberdeen, Aberdeenshire AB15 8JJ (GB).

(74) Common Representative: **THE PROCTER & GAMBLE COMPANY**, c/o Mr. T. David Reed, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US)

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(54) Title: **COMPOSITIONS SUITABLE FOR THE TREATMENT OF HAIR COMPRISING CHELANTS AND METHODS FOR REDUCING OXIDATIVE HAIR DAMAGE**

(57) Abstract: The present invention relates to hair care compositions comprising an oxidizing agent and chelants having a $\log K_{CuL}/\log K_{CaL}$ ratio calculated at pH 10 of at least 3.20 wherein $\log K_{CuL}$ is the common logarithm of the Conditional Stability Constant of said chelant with Cu^{2+} and $\log K_{CaL}$ is the common logarithm of the Conditional Stability Constant of said chelant with Ca^{2+} . Suitable chelants are diamine- N,N' -dipolyacids or monoamine monoamide- N,N' -dipolyacids. The compositions according to the present invention contribute to reducing the oxidative damage sustained by a keratinous fiber such as hair during bleaching, dyeing, perming or other oxidative treatments. Especially preferred diamine dipolyacid is ethylenediamine- N,N' -disuccinic acid (EDDS).

COMPOSITIONS SUITABLE FOR THE TREATMENT OF HAIR COMPRISING CHELANTS AND METHODS FOR REDUCING OXIDATIVE HAIR DAMAGE

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FIELD

The present invention relates to hair care compositions comprising specific chelants and methods for reducing oxidative hair damage during oxidative treatments of hair such as bleaching, oxidative dyeing or perming.

BACKGROUND

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Melanin is a natural pigment found in hair. Melanin and hair-forming cells are naturally produced in the hair bulb at the root of the hair. As new cells are produced, the older ones are pushed upwards out of the skin to form the hair shaft, which is the part of the hair that can be seen above the scalp. Hair can be schematically described as being made of a center part called the cortex, which contains the melanin, and an outer layer called the cuticle. It is the cortex that gives hair its special qualities such as elasticity and curl.

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The hair shaft is made of dead cells that have turned into a mixture of different forms of the special hair protein, keratin. Keratin contains high concentrations of a particular amino acid called cystine. Every cystine unit contains two cysteine amino acids in different chains, which have come to lie near each other and are linked together by two sulphur atoms, forming a very strong chemical bond known as a disulphide linkage. This cross-linking by disulphide linkages between the keratin chains accounts for much of the strength of the hair.

20

Bleaching and dyeing (or coloring) of hair has become increasingly popular over the past years. Younger people may want to change the natural color of their hair to a more fashionable one, while older people may also use dyeing compositions to conceal gray hair. As people grow older, the production of melanin slows, giving more and more gray hair over time. Melanin can be purposely altered by chemical treatments to give lighter shades. The lightening is

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achieved by oxidizing the melanin pigments, usually with an oxidizing agent in alkaline solution, also called bleaches. Examples of oxidizing agents that can be used are hydrogen peroxide, potassium, sodium or ammonium salts of perborate or percarbonate, persulfate and percarbamide.

5 Bleaches are also used during oxidative dyeing treatments. Oxidative (or "permanent") dye compositions comprise "precursor dyes" which are small molecules capable of diffusing into the hair. These molecules mainly belong to three classes of aromatic compounds: diamines, aminophenols and phenols. They are sufficiently small to diffuse in the hair shaft where, once activated by an oxidizing agent such as hydrogen peroxide, they further react with other
10 precursors to form larger colored complexes. Oxidative hair dye compositions commonly contain, in addition to the dye precursors and a source of peroxide, a variety of additional cosmetic and peroxide stabilizing agents.

 Oxidizing agents can activate oxidative dye precursors across a range of
15 pH. However, it is known that enhanced dye oxidation can be achieved via the use of a hair-swelling agent (HSA) that can adjust the pH of the oxidizing solution. Such HSA's further enhance the oxidizing and dyeing process by swelling the hair fibers to aid both the diffusion of the peroxide and dyeing agents into the hair and enabling faster, more thorough dye oxidization and hair
20 dyeing. Preferred hair-swelling agents for adjusting the pH of peroxide hair oxidizing compositions are aqueous alkaline solutions containing ammonia (ammonium hydroxide) or monoethanolamine(MEA).

 Low levels of chelants are routinely used as stabilizers or preservatives in various oxidizing compositions. For example, EDTA (ethylenediaminetetraacetic
25 acid) is commonly used as a stabilizer in hydrogen peroxide solution, which would otherwise decompose too rapidly and could not be stored for a long time. Ethylene diaminedissuccinic acid (EDDS) is also known as a good stabilizing agent component to increase the stability of laundry bleaching products. Amounts as low as 0.1% by weight of the oxidizing composition are usually used
30 to stabilize the oxidizing agent contained in said oxidizing compositions.

Oxidative treatments of hair such as bleaching (decoloration) and oxidative dyeing give good results and are very commonly used. They are however not without drawbacks. The oxidizing agents used for bleaching and oxidative dyeing damage hair to some extent. The mechanism by which damage is caused to the hair fibers is not perfectly understood. However, it is known that some of the disulphide bonds linking the keratin chains break in the presence of oxidizing compositions. Repeated oxidative treatments leave weak, brittle hairs, which have little shine and luster. An enormous effort has been made to address this problem over the past years, and various solutions have been proposed.

Today, most dyeing or bleaching compositions are sold with a conditioner, which is applied on hair after the bleaching or dyeing composition has been rinsed off. Examples of conditioning agents are silicones, cationic surfactants and cationic polymers. However efficient, conditioners cannot prevent successive chemical treatments causing premature hair breakage. In fact, conditioners do not bring the hair back to its initial condition but merely conceal the damage under a protective layer of the conditioning agent, which only results in an improved feel of the hair.

Attempts have been made to protect the hair from damage instead of merely concealing it. US 5,100,436 discloses hair dyeing compositions comprising metal-chelant complexes. The use of catalytic amounts of dipyriddy or o-phenanthroline complexes (0.001 to 0.1% by weight of the solution) allows a reduction in the time of exposure, thus reducing the damage caused by the oxidizing agent.

US 6,013,250 discloses composition for treating hair against chemical and photo damage by the use of hydrolyzed proteins having an abundance of anionic amino acids and in particular, sulphur-containing amino acids. These proteins serve as "decoys", in order to minimize the damage caused to the natural disulphide bonds.

US4,138,478 discloses agents for reducing the damage to hair during bleaching and dyeing by the use of a water-soluble 3-amino-1-hydroxypropane-1,1-diphosphonic compound for protecting hair from damage by "nascent

oxygen". According to this patent, "the diphosphonic compound is substantively adsorbed by the hair and acts to hinder degradation of the hair by nascent oxygen which is either present therewith or which is substantially added". Other protective compounds such as hydroxyethane-1,1 diphosphonic acid (HEDP) and ethylenediaminetetramethylene phosphonic acid (EDTMP) are disclosed at low levels in US3,202,579 and US3,542,918.

"Properties of peroxide-bleached hair" (W.Edman & E.Marti, J. Soc. Cosmet. Chem., 1960, p.133), discloses that an aqueous solution of hydrogen peroxide is stabilized by adding 0.1% by weight of the bleaching composition of tetrasodium salt of EDTA (ethylenediamine tetraacetic acid) and that damage to hair can be prevented by adding 0.1% of the tetrasodium salt of EDTA to the aqueous bleaching compositions. However, it has now been surprisingly found that EDTA, although widely used in bleaching and dyeing compositions, displays very little benefits, unless utilized at levels much higher than 0.1%.

Chelants in hair care compositions have been used to remove minerals bound to hair. For example, US 5,635,167 discloses a process for the removal of exogenous metal ions that have become attached to hair. The treatment comprises a step wherein hair is contacted with a blend of chelating agents (selected from the group consisting of amino acid chelating agents, polyphosphate chelating agents and phosphonate chelating agents) at a pH of between 4 and 9 and at a concentration of between 4% to 25% by weight.

WO97/24106, Dias et al. discloses hair coloring compositions comprising a water soluble peroxygen-bleach, a bleaching aid selected from organic peroxyacid bleach precursors and preformed organic peroxyacids and one or more hair coloring agents. Various chelants are disclosed as optional ingredients and exemplified in hair care compositions at 0.1% by weight of the composition. The organic peroxy acid bleach precursors are defined as organic compounds that react with hydrogen peroxide in a perhydrolysis reaction to produce a peroxyacid. These bleaching aids are claimed to provide benefits including reduced hair damage at lower pH. However, the Applicant has found that at a pH higher than 8, these bleaching aids are much more damaging to hair than usual

water-soluble oxidizing agents such as hydrogen peroxide. Without being bound by theory, the Applicant believes that the conjugate base of the organic peroxyacid formed at a pH above 8 is more likely to oxidize the disulphur bonds of the keratin than other oxidizing agents such as hydrogen peroxide.

5 Additionally, hair coloration, especially with oxidative dyes is much poorer at pH 8 than pH 10, which is another advantage of this invention over WO9724106. Finally peroxyacid precursors are difficult to solubilize, especially in oil-in-water emulsion.

10 Despite these developments, damage to hair caused by the strongly aggressive chemicals contained in most bleaching, dyeing or perming compositions particularly with repeated usage is still a problem, particularly at high pH.

15 It is hence an object of the present invention to provide new compositions capable of improved protection of keratinous fibers such as human hair from oxidative damage, in particular the structurally important keratin bonds such as the disulphide bonds from oxidative breakage.

It is another object of this invention to provide bleaching, dyeing or perming compositions with a better efficiency in terms of light shade, color evenness, color fading and hair feel.

20 It is another object of this invention to provide a hair-protecting agent that is non-toxic, even when utilized in relatively large proportions and which is biodegradable.

25 The Applicant has surprisingly found that chelants having specific Conditional Stability Constants for Copper and Calcium at pH 10 have damage inhibiting properties. The Applicant has also found that diamine-N,N'-dipolyacid or monoamine monoamide-N,N'-dipolyacid chelants were particularly useful at reducing hair damage. None of the above-mentioned references disclose the compositions of the present invention.

SUMMARY

The subject of the present invention relates to a composition suitable for treating hair comprising:

a) an oxidizing agent; and

b) a chelant (L) having a $\frac{\log K_{CuL}}{\log K_{CaL}}$ ratio calculated at pH 10 of at least

5 3.20, preferably at least 3.30, more preferably at least 3.40, even more preferably at least 3.50;

wherein $\log K_{CuL}$ is the common logarithm of the Conditional Stability Constant of said chelant with Cu^{2+} and $\log K_{CaL}$ is the common logarithm of the Conditional Stability Constant of said chelant with Ca^{2+} .

10 Preferred chelants furthermore have a Hydrogen Peroxide Decomposition Ratio (% Loss) of less than 3.5 as measured by the Hydrogen Peroxide Decomposition Ratio Measurement Protocol described herein and/or forms a hexadendate complex with Cu^{2+} .

Suitable chelants are diamine-N,N'-dipolyacids and monoamine
15 monoamide-N,N'-dipolyacids.

DETAILED DESCRIPTION

While the specification concludes with claims which particularly point out and distinctly claim the invention, it is believed the present invention will be better understood from the following description.

20 As used herein the term "hair" to be treated may be "living" i.e. on a living body or may be "non-living" i.e. in a wig, hairpiece or other aggregation of non-living keratinous fibers. Mammalian, preferably human hair is preferred. However wool, fur and other keratin containing fibers are suitable substrates for the compositions according to the present invention.

25 As used herein, the term "oxidizing composition" means a composition comprising at least one oxidizing agent suitable for use on hair, such as hydrogen peroxide, sodium, potassium, ammonium or other salts of perborate, percarbonate, persulfate and percarbamide. Examples of such compositions are oxidative dye compositions and bleaching compositions.

As used herein the term "oxidative treatment of hair" or a "hair treatment comprising at least one oxidative step" is used in the broad sense in that it is intended to encompass all treatments of hair comprising at least one step of contacting hair with at least one oxidizing composition. Non-limiting examples of such compositions are oxidative dye compositions and bleaching compositions.

As used herein the term "immediately" means within about 1 hour, preferably within about 30mn, more preferably within about 15mn.

As used herein the term "log x" refers to the common (or decimal) logarithm of x.

All percentages are by weight of the total composition unless specifically stated otherwise. When more than one composition are used during a treatment, the total weight to be considered is the total weight of all the compositions applied on hair simultaneously (i.e. the weight found "on head") unless otherwise specified. All ratios are weight ratios unless specifically stated otherwise.

All cited references are incorporated herein by reference in their entireties. Citation of any reference is not an admission regarding any determination as to its availability as prior art to the claimed invention.

Chelants

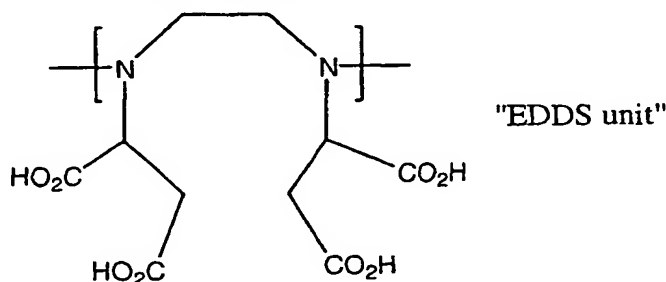
Definition

The term "chelant" (or "chelating agent" or "sequestering agent") is well known in the art and refers to a molecule or a mixture of different molecules each capable of forming a chelate with a metal ion. A chelate is an inorganic complex in which a compound (chelant) is coordinated to a metal ion at two or more points so that there is a ring of atoms including the metals. Chelants contain two or more electron donor atoms that form the coordination bonds with the metal ion.

Chelants are well known in the art and a non-exhaustive list thereof can be found in AE Martell & RM Smith, Critical Stability Constants, Vol. 1, Plenum Press, New York & London (1974) and AE Martell & RD Hancock, Metal

Complexes in Aqueous Solution, Plenum Press, New York & London (1996) both incorporated herein by reference.

When related to chelants, the terms "salts and derivatives thereof" mean all salts and derivatives comprising the same functional structure (same chemical backbone) as the chelant they are referring to and that have similar or better chelating properties. These terms include alkali metal, alkaline earth, ammonium, substituted ammonium salts (e.g. monoethanolammonium, diethanolammonium, triethanolammonium), esters of chelants having an acidic moiety and mixtures thereof, in particular all sodium, potassium or ammonium salts. The term "Derivatives" also includes "chelating surfactant" compounds (these are chelants modified to bear a surfactant moiety while keeping the same chelating functionality, see US5284972, "N-acyl-N,N',N'-ethylenediaminetriacetic acid" for an example of modified ethylenediaminetriacetic acid. The term "Derivatives" also includes large molecules comprising one or more chelating groups having the same functional structure as the parent chelants. Examples of these large molecules include polymeric EDDS (ethylenediaminedisuccinic acid) made of unit block according to the following structure:



and disclosed in US5,747,440 Kellett et al.

Damage prevention

The Applicant has surprisingly found that chelants having a stronger affinity for transition metal ions such as Cu^{2+} than for alkaline-earth metal ions such as Ca^{2+} at pH10 efficiently prevent oxidative hair damage. This is particularly true for formulations with rheologies greater than water such as oil-in-water emulsions or thickened aqueous solutions.

Conditional Stability Constants of preferred chelants

The relative affinity of a chelant for Cu^{2+} versus Ca^{2+} can be assessed by calculating the ratio of the log of the Conditional Stability Constant of the chelant for Cu^{2+} to the log of the Conditional Stability Constant of the chelant for Ca^{2+} at pH 10 as described below.

The Conditional Stability Constant is a parameter commonly used in the art to practically assess the stability of metal-chelant complex at a given pH. A detailed discussion on Conditional Stability Constant can be found for example in "Dow chelating agents" published by the Dow Chemical Company Limited, incorporated herein by reference.

The Stability constant of a metal chelant interaction is defined as:

$$K_{ML} = \frac{[ML]}{[M][L]}$$

Where:

[ML] = Concentration of metal chelant complex at equilibrium

[M] = Concentration of free metal ion

[L] = Concentration of free chelant

K_{ML} = Stability constant for the metal chelant complex

Wherein all concentrations are expressed in mol/dm^3 . Stability constants are conveniently expressed as logarithms. The values of the logarithms of the Stability constant values for some exemplary metal ion - chelant complexes are given in the following table:

Table 1 - Log Stability constants for 1:1 complexes of various chelants with Cu and Ca [1] (fully deprotonated chelants)

<u>Agent</u>	<u>log K*</u>	
	<u>Cu</u>	<u>Ca</u>
EDDS	18.35	4.58
DTPMP	19.5	7.1
EDTMP	23.2	9.36
DTPA	21.4	10.75

HEDP	11.84	6.0
EDTA	18.78	10.65
EDDHA	25.3	7.2

* All measured at 25deg and 0.1M ionic strength

Most chelants have a degree of protonation that is dependent on pH. This can be expressed using chelant proton Stability constants (stepwise K)

These Stability constants are obtained from the equation below:



The values of the proton chelant Stability constant for some usual chelants are given in the tables below:

Table 2a - log protonation constants for tetra-protonated chelants [1]

	HL^{3-}	H_2L^{2-}	H_3L^{-}	H_4L
EDDS ⁴⁻	10.01	6.84	3.86	2.95
HEDP ⁴⁻	10.8	6.88	2.53	1.8
EDTA ⁴⁻	10.19	6.13	2.69	2.00
EDDHA ⁴⁻	12.1	9.5	8.5	6.3

Table 2b - log protonation constants for penta-protonated chelants [1]

	HL^{4-}	H_2L^{3-}	H_3L^{2-}	H_4L^{-}	H_5L
DTPA ⁵⁻	10.48	8.60	4.28	2.6	2.0

Table 2c - log protonation constants for hepta-protonated chelants [1]

	HL^{6-}	H_2L^{5-}	H_3L^{4-}	H_4L^{3-}	H_5L^{2-}	H_6L^{-}	H_7L
EDTMP ⁷⁻	13.0	9.78	7.94	6.42	5.17	3.02	1.30

Table 2d - log protonation constants for octa-protonated chelants [1]

	HL^{7-}	H_2L^{6-}	H_3L^{5-}	H_4L^{4-}	H_5L^{3-}	H_6L^{2-}	H_7L^{-}	H_8L
DTPMP ⁸⁻	12.0	10.10	8.15	7.17	6.38	5.50	4.45	2.8

[1] = Arthur Martell & Robert M Smith, Critically Selected Stability Constants of Metal Complexes Database, Version 3.0

The stability constants of chelant-metal ion complexes are well documented in the literature for commonly used chelants (see for example = Arthur Martell & Robert M Smith, Critically Selected Stability Constants of Metal Complexes Database, Version 3.0 and above, incorporated herein by reference). When not documented the constants can still be measured using various analytical methods (see "Metal Complexes in Aqueous Solutions", Martel and Hancock, edition Modern Inorganic Chemistry, p.226-228, incorporated herein by reference).

The gradual change in chelant species as pH changes can be represented using alpha coefficients (α_{HL}), defined as

$$\text{Alpha coefficient (at a given pH)} = \frac{\text{Total concentration of ligand}}{\text{Free ligand concentration}}$$

In the case of tetra-acid chelants the values can be calculated from

$$\alpha_{HL} = 1 + K_1[H] + K_1K_2[H]^2 + K_1K_2K_3[H]^3 + K_1K_2K_3K_4[H]^4$$

A further factor affecting metal chelant interactions is the tendency of metals to form hydroxide species as the pH increases. This effect can be represented using metal alpha values [2] as summarised in the table below at pH 10:

Table 3 - log alpha values for metal ions [2]

pH	Ca ²⁺	Cu ²⁺
10	0.0	2.00

[2] = A Ringbom & E Wanninen, Treatise on Analytical Chemistry, 2nd Ed, 1979, Part 1, Vol 2

By combining Stability constants and alpha constants at pH 10 we can use the formula below to give the effective chelating power of a chelant. This is the Conditional Stability Constant referred to herein.

$$K_{ML}(\text{cond}) = \frac{K_{ML}}{\alpha_M \cdot \alpha_{HL}} \quad \log K_{ML}(\text{cond}) = \log K_{ML} - \log \alpha_{HL} - \log \alpha_M$$

A detailed discussion on Conditional Stability Constant can be found for example in "Dow chelating agents" published by the Dow Chemical Company Limited, incorporated herein by reference. The data for a range of chelants with Cu and Ca is given below:

5

<u>Chelant</u>	<u>log Conditional Stability Constant (pH 10)</u>		
	<u>Cu</u>	<u>Ca</u>	<u>Ratio Cu/Ca</u>
EDDHA	21.04	4.97	4.23
EDDS	16.04	4.27	3.76
DTPMP	15.14	4.74	3.19
EDTMP	17.99	6.15	2.92
DTPA	18.78	10.13	1.85
HEDP	8.98	5.13	1.75
EDTA	16.37	10.24	1.60

The applicant has surprisingly found that levels as low as 0.1% by weight of chelants having a ratio $\frac{\log K_{CuL}}{\log K_{CaL}}$ of at least 3.20 give good oxidative damage

protection (wherein $\log K_{CuL}$ is the common logarithm of the Conditional Stability Constant between this chelant and Cu^{2+} and wherein $\log K_{CaL}$ is the common logarithm of the Conditional Stability Constant between this chelant and Ca^{2+} , both at pH 10) This $\frac{\log K_{CuL}}{\log K_{CaL}}$ ratio should preferably be at least 3.30,

more preferably at least 3.40, even more preferably at least 3.50 at pH 10. It is important to calculate this ratio at pH 10, because oxidizing compositions for treating hair usually have a pH of from 8 to 12. Using stability constants without taking into account the influence of the pH is a common mistake and will give misleading results for the purpose of identifying chelants that will prevent oxidative damage at low levels.

Levels of such chelants in the oxidizing compositions or in the pre-treat compositions can be as low as about 0.1% but will preferably at least about

0.25%, more preferably at least about 0.5%, even more preferably at least about 1% by weight of the composition. Levels as high as about 10% can be used, but above this level significant formulation and/or human safety concerns may arise. Levels above about 4% can be used but will usually not result in additional damage benefit.

Hydrogen Peroxide Decomposition Ratio (%Loss)

It is preferred that the complexes formed by these preferred chelants efficiently inhibit the red-ox chemistry of Cu^{2+} . The ability of chelants to inhibit the red-ox chemistry of the chelated copper metal ion can be effectively compared using their Hydrogen Peroxide Decomposition Ratio (% Loss) as measured by the Hydrogen Peroxide Decomposition Ratio Measurement Protocol described hereafter in the "EXPERIMENTALS" section.

The table below shows the Hydrogen Peroxide Decomposition Ratio (% Loss) for different chelants:

Chelant	Peroxide % at t=0	Peroxide % at t=30mn	% Loss
EDTA	3.576	3.573	0.1%
EDDS	3.150	3.104	1.5%
DTPMP	3.078	2.964	3.7%
MGDA	3.498	3.104	11.3%
HEDP	4.126	2.792	32.3%
No chelant	0.563	-	100%

MGDA is methylglycinediacetic acid and forms a pentadentate complex with Cu^{2+} .

Chelants having a Hydrogen Peroxide Decomposition Ratio (% Loss) of less than 10% are preferred for use herein. Preferably the value of the Hydrogen Peroxide Decomposition Ratio is less than 3.5%, more preferably less than 3%, even more preferably less than 2.0%.

Chelants forming hexadentate type complexes with Cu^{2+} were found to adequately inhibit the red-ox chemistry of the metal ion ("hexadentate complex" means that the chelant forms six bonds with the chelated metal ion). Examples of chelants that form such complexes with Cu^{2+} are EDDS, HBED, EDTA and

EDDHA. Forming such complexes efficiently prevents the chelated heavy metal ion from reacting with the molecule of the oxidizing agent, for example hydrogen peroxide.

As the table above shows, EDTA has a very good capacity at inhibiting the red-ox chemistry of copper. This was a very surprising finding for the inventors because experiments had shown that EDTA had very poor damage prevention properties in "real" conditions of use wherein the concentration of transition metal ion such as copper and alkaline-earth metal ion such as Ca^{2+} are high compared to lab-condition wherein the water is de-ionized for experiments. (see EXPERIMENTALS hereinbelow). The Applicant believes that this clearly shows that the ratio $\frac{\log K_{\text{CuL}}}{\log K_{\text{CaL}}}$ at pH 10 is an essential parameter to use in order to determine the oxidative damage prevention efficiency of chelants in real conditions of use.

Without being bound by theory, it is believed that the above-mentioned preferred chelants act to chelate environmental and intrinsic heavy metal ions such as iron, manganese and copper. In the absence of chelants, these heavy metal ions react with hydrogen peroxide to give highly damaging species such as free radicals, which are believed to be very harmful to the disulphide bonds of hair. It is believed that alkaline-earth metal ions such as Ca^{2+} compete with heavy metal ions to form complexes with the chelants, therefore chelants with a much higher affinity for Cu^{2+} than for Ca^{2+} will much more efficiently prevent oxidative damage than chelants with a lower relative affinity for Cu^{2+} . The Applicant believes that the importance of measuring damage under real life conditions (i.e. at pH10 and with non-deionized water) was never recognized or foreseen until now.

Examples of preferred chelants

The following compounds illustrate chelants providing excellent damage protection, even at levels as low as 0.1% by weight of the oxidizing composition. Higher levels of at least about 0.25%, at least about 0.5%, or even at least about

1% by weight of the composition can also be used for even better damage benefits. Levels above about 4% can be used but will usually not result in additional damage benefit.

Preferred chelants according to the present invention are aminocarboxylic acid chelants. Carboxylic acid chelants as defined herein are chelants having at least one carboxylic acid moiety (-COOH).

Preferred aminocarboxylic chelants are diamine-N,N'-dipolyacid and monoamine monoamide-N,N'-dipolyacid chelants, salts thereof and derivatives thereof. Preferred polyacids contain at least two acid groups independently selected from the carboxylic acid group (-COOH), sulphonic group (-SO₃H), the o-hydroxyphenyl group, the m-hydroxyphenyl group and the p-hydroxyphenyl group. Suitable polyacids include diacids, triacids and tetraacids, preferably diacids. Preferred salts include alkali metal, alkaline earth, ammonium or substituted ammonium salts. EDTA is a tetramonoacid and does not belong to this class of preferred chelants.

Preferably, the polyacids are di-carboxylic acids, preferably di-carboxylic acids having a carbon chain length of from about 3 to about 10 carbon atoms, more preferably from about 4 to about 6 carbon atoms, even more preferably about 4 carbon atoms.

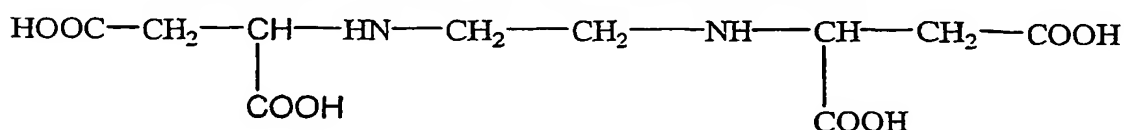
Preferred for use herein are diamine-N,N'-dipolyacids and monoamine monoamide-N,N'-dipolyacids wherein the polyacid species is a diacid, preferably a diacid having a carbon chain length of from about 3 to about 10 carbon atoms, more preferably from about 4 to about 6 carbon atoms, even more preferably about 4 carbon atoms.

Exemplary diamine dipolyacids suitable for use herein include ethylenediamine-N,N'-disuccinic acid (EDDS), ethylenediamine-N,N'-diglutamic acid (EDDG), 2-hydroxypropylenediamine-N,N'-disuccinic acid (HPDDS), all disclosed in European Patent EP0687292, ethylenedicysteic acid (EDC) disclosed in US5,693,854, diaminoalkyldi(sulfosuccinic acids) (DDS) disclosed in US5,472,642 and EDDHA (ethylenediamine-N,N'-bis(ortho-hydroxyphenyl acetic acid)), a method of preparation of which is disclosed in EP331556. A preferred

monoamine monoamide-N,N'-dipolyacid is glycine-N,N'-disuccinic acid (GADS), described in US 4,983,315.

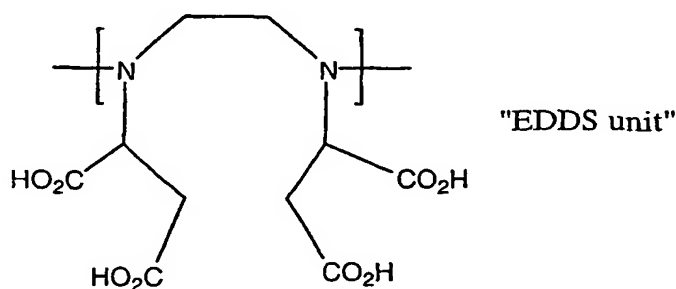
Highly preferred for use herein is ethylenediamine-N,N'-disuccinic acid (EDDS), derivatives and salts thereof. Preferred EDDS compounds for use herein are the free acid form, and salts thereof. Preferred salts include alkali metal, alkaline earth metals, ammonium and substituted ammonium salts (e.g. monoethanolammonium, diethanolammonium, triethanolammonium). Highly preferred salts are sodium, potassium, magnesium and calcium salts. Examples of such preferred sodium salts of EDDS include Na₂EDDS and Na₃EDDS.

The structure of the acid form of EDDS is as follows:



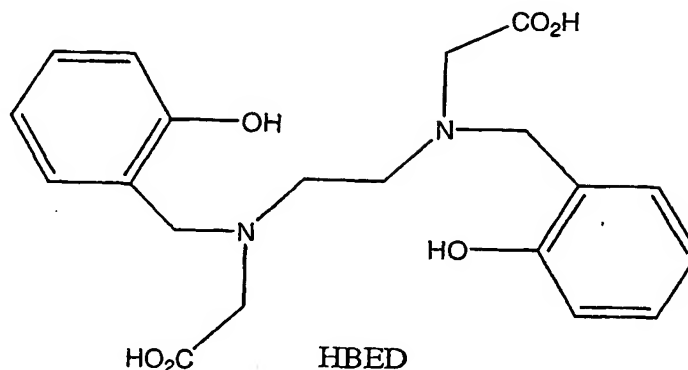
EDDS can be synthesised, for example, from readily available, inexpensive starting materials such as maleic anhydride and ethylenediamine. The synthesis of EDDS from maleic anhydride and ethylene diamine yields a mixture of three optical isomers, [R,R], [S,S], and [S,R] (25% S,S, 50% R,S and 25% R,R), due to the two asymmetric carbon atoms. The biodegradation of EDDS is optical isomer-specific, with the [S,S] isomer degrading most rapidly and extensively.

US5,747,440, Kellett et al., discloses EDDS derivatives comprising an modified polyamine having units of the formula:



Preferred chelants that are not diamine-N,N'-dipolyacid and monoamine monoamide-N,N'-dipolyacid chelants include N,N'-bis(2-

hydroxybenzyl)ethylenediamine-N,N'-diacetic acid (HBED) salts thereof and derivatives thereof:



Examples of suitable HBED derivatives can be found in WO9744313, assigned to Novartis.

Oxidizing agent

The compositions according to the present invention comprise or are used in combination with a composition that comprises at least one oxidizing agent. Preferred oxidizing agents for use herein are water-soluble peroxygen oxidizing agents. "Water-soluble" as defined herein means that in standard condition at least 0.1g, preferably 1g, more preferably 10g of said oxidizing agent can be dissolved in 1 liter of deionized water. The oxidizing agents are valuable for the initial solubilisation and decolorisation of the melanin (bleaching) and accelerate the polymerization of the oxidative dye precursors (oxidative dyeing) in the hair shaft.

Preferred water-soluble oxidizing agents are inorganic peroxygen materials capable of yielding hydrogen peroxide in an aqueous solution. Water-soluble peroxygen oxidizing agents are well known in the art and include hydrogen peroxide, inorganic alkali metal peroxides such as sodium periodate and sodium peroxide and organic peroxides such as urea peroxide, melamine peroxide, and inorganic perhydrate salt bleaching compounds, such as the alkali metal salts of perborates, percarbonates, perphosphates, persilicates, persulphates and the like. These inorganic perhydrate salts may be incorporated as monohydrates, tetrahydrates etc. Mixtures of two or more such oxidizing

agents can be used if desired. Preferred for use in the compositions according to the present invention is hydrogen peroxide.

In conventional dyeing and bleaching compositions, levels of peroxygen oxidizing agent are usually of from about 0.1% to about 7% by weight. Higher
5 levels, whilst giving good results in term of efficacy were until now not practical because of increased hair damage. The oxidative damage protection provided by the present invention makes it now possible to use oxidizing agent such as hydrogen peroxide in level up to 40% in the oxidizing composition. However, for safety reasons, level above 12% should be carefully investigated before being
10 used on human. Preferably, the level of the oxidizing agent in the oxidizing composition is of from about 0.5% to about 20% by weight, more preferably of from about 1% to about 15%. The compositions according to the present invention provide excellent gray coverage, vibrant colors and acceptable damage at level above about 7% (typically about 12%).

15 The weight ratio of oxidizing agent to oxidative damage inhibiting chelant (e.g. EDDS) is preferably in the range of from 50:1 to 1:50, preferably from 25:1 to 1:25, more preferably from 15:1 to 1:15, even more preferably of from 9:1 to 1:10.

Additional components

20 Moreover, it is also intended that the compositions of the present invention may be complex compositions, which in addition to the chelant and oxidizing agent comprise other components that may or may not be active ingredients. This includes, but is not limited to, buffering agents, hair dyeing agents such as oxidative dye precursors, non-oxidative dyes, thickeners, solvents, enzymes,
25 anionic, non ionic, amphoteric and cationic surfactants, conditioning agents, carriers, antioxidants, stabilizers, perming actives, perfume, hair swelling agents and/or polymers. Some of these additional components are detailed hereafter.

It can be however suitable that the composition according to the present invention should be preferably substantially free from organic peroxyacid
30 precursors and preformed organic peroxyacid, such as those defined in

WO97/24106. These include sodium nonanoylbenzenesulfonate (NOBS), acetyltriethylcitrate (ATC), sodium (6-nonaamidocaproyl)oxybenzenesulfonate, peracetic and peroxanoic acid and can have a negative effect on the efficiency of bleaching and coloring and increase damage at a pH above 8. The term
5 substantially free as used herein means that the compositions according to the present invention should comprise less than 1.5%, preferably less than 1%, more preferably less than 0.5% and even more preferably less than 0.1% by weight of the composition of such compounds.

Finally, the compositions according to the present invention can be
10 provided in any usual form, such as for example an aqueous composition, a powder, a gel or an oil-in-water emulsion. Preferred media for the compositions according to the present invention are thickened aqueous solutions comprising a salt-tolerant thickener or oil-in-water emulsions.

pH buffering agents

15 The compositions according to the present invention preferably further comprise a pH buffering agent. The pH of the composition is preferably of from about 8 to about 12, more preferably of from about 9 to about 11, even more preferably of from about 9.5 to about 10.5. Suitable buffering agents are well known in the art and include for example ammonia/ammonium acetate mixture
20 and monoethanolamine (MEA).

Oxidative hair dye precursors

These compounds are well known in the art, and include aromatic diamines, aminophenols and their derivatives (a representative but not exhaustive list of oxidation dye precursor can be found in Sagarin, "Cosmetic
25 Science and Technology", "Interscience, Special Edn. Vol. 2 pages 308 to 310). Precursors can be used with couplers. Couplers are generally colorless molecules that can form colors in the presence of activated precursors.

The choice of precursors and couplers will be determined by the color, shade and intensity of coloration that is desired. The precursors and couplers

can be used herein, singly or in combination, to provide dyes having a variety of shades ranging from ash blonde to black.

Hair dye compositions will generally comprise from about 0.001% to about 10%, preferably from about 0.1% to about 2%, of oxidative dye precursors and couplers.

Thickeners

The composition of the present invention may optionally further comprise at least about 0.1% of thickeners. Thickeners are preferably comprised in amount sufficient to provide the composition with a viscosity of from about 1 Pa.s to 10 Pa.s (1,000 to 10,000 cP) at 26°C in order to provide a composition that can be readily applied to the hair without dripping.

Preferred for use herein are salt tolerant thickeners. Salt-tolerant thickeners are functionally defined herein as compounds that increases the viscosity of an aqueous composition consisting of 3.8% DTPMP (tetrasodium salt) and 1.95% NH_3 to at least 1 Pa.s (1,000 cP) when incorporated at levels of 2% by weight as measured at 26.7°C. The viscosity can be measured with a Brookfield viscometer DVII, using S41 spindles for samples under 10 Pa.s (10,000 cP) and spindle S52 for samples over 10 Pa.s (10,000 cP) (available from Brookfield), with a speed rating of 1 revolution per minute and samples sizes of 2ml (for S41 spindle) or 0.5 ml (for S52 spindle).

A non exclusive list of suitable salt tolerant thickeners for use herein include xanthan, guar, hydroxypropyl guar, scleroglucan, methyl cellulose, ethyl cellulose (commercially available as Aquacote®), hydroxyethyl cellulose (Natrosol®), carboxymethyl cellulose, hydroxypropylmethyl cellulose, microcrystalline cellulose, hydroxybutylmethyl cellulose, hydroxypropyl cellulose (Klucel®), hydroxyethyl ethyl cellulose, cetyl hydroxyethyl cellulose (Natrosol® Plus 330), N-vinylpyrrolidone (Povidone®), Acrylates / Ceteth-20 Itaconate Copolymer (Structure® 3001), hydroxypropyl starch phosphate (Structure® ZEA), polyethoxylated urethanes or polycarbamyl polyglycol ester (e.g. PEG-150/Decyl/SMDI copolymer = Aculyn® 44, PEG-150/Stearyl/SMDI copolymer =

Aculyn 46®), trihydroxystearin (Thixcin®) acrylates copolymer (e.g. Aculyn® 33) or hydrophobically modified acrylate copolymers (e.g. Acrylates / Steareth-20 Methacrylate Copolymer = Aculyn® 22).

Fatty alcohols have thickening properties and can be used in the compositions of present invention. Fatty alcohols are however not salt-tolerant thickeners according to the above definition. A mixture of 2% cetyl and stearyl alcohol has for example a viscosity of less than about 0.7 Pa.s (700 cP) as measured at 26°C with a Brookfield viscometer in the conditions disclosed hereabove.

Conditioning agent

The compositions of the present invention preferably, but not necessarily, further comprises at least one conditioning agent. Preferred conditioning agents are selected from silicone materials, especially nonvolatile silicone and amino functionalised silicones, cationic surfactants, cationic polymers and mixtures thereof.

The conditioning agent will generally be used at levels of from about 0.05% to about 20% by weight of the composition, preferably of from about 0.1% to about 15%, more preferably of from about 0.2% to about 10%, even more preferably of from about 0.2% to about 2%. The minimum level that is used in a particular composition should be effective to provide a conditioning benefit. The maximum level that can be used is not limited by theory, but rather by practicality. It is generally unnecessary and expensive to use levels in excess of about 10% and, depending on the type of agent (polymeric conditioners being most prone), such high levels can cause an undesirable weighting down of the hair.

Suitable conditioning agents are disclosed in WO9804237 p.22-p.29, and in WO9632919 p.17-22 both incorporated herein by reference.

EXPERIMENTALS

All results discussed herein were obtained by testing chelants according to the following protocols. The chelants tested can be obtained from any usual supplier.

Hydrogen Peroxide Decomposition Ratio Measurement Protocol

5 The Hydrogen Peroxide Decomposition Ratio Measurement Protocol is defined as follows: 6.0% by weight of concentrated ammonium hydroxide (30% active ammonia) is added to deionised water and the pH of the solution is adjusted to 10 using acetic acid. 300ppm of copper sulphate and 0.026M of the chelant to be tested are added to said composition. 10ml of this solution is then
10 mixed with 1ml of hydrogen peroxide (35% active). The initial level of hydrogen peroxide is measured at this moment (t=0); the final level of hydrogen peroxide is measured after 30 minutes. The value of the ratio of the hydrogen peroxide concentration at t=0 and at t=30mn is the Hydrogen Peroxide Decomposition Ratio (% Loss).

15 The initial and final level of hydrogen peroxide can be measured according to any standard technique. The following is a well-known and standard technique that was used by the inventors: 0.2 - 0.3g (the exact quantity being precisely measured) of the solution to be titrated is added to 40ml of 10% acetic acid. The autotitrator (Mettler DL58 Autotitrator) adds 20ml of potassium iodide
20 solution (15% in water), 5ml of ammonium molybdate solution (2% in water) and titrates (while stirring) with 0.1M sodium thiosulphate solution. The level of hydrogen peroxide (% Peroxide) is then calculated from the following equation:

$$\% \text{Peroxide} = \frac{\text{end - point (in ml)} \times \text{molarity of sodium thiosulphate} \times 34.02}{2 \times 10 \times \text{sample weight (in g)}}$$

34.02 being the molecular weight of Hydrogen Peroxide.

25 Three replicate runs are made at both t = 0 and t = 30mn and then averaged to calculate the Hydrogen Peroxide Decomposition Ratio (% Loss).

Oxidative Hair Treatment Protocol

For each chelant tested, seven switches of virgin dark hair were used. "Virgin hair" means hair that has never been treated chemically and can be

bought, for example, at Hugo Royer International Ltd, 10 Lakeside Business Park, Swan Park, Sandhurst, Berkshire, GU47 9ND. The switches usually weighed about 1.5g each and are treated stepwise according to the following protocol.

- 5 A bleaching composition comprising the chelant to be tested is prepared by mixing in equal weight amounts a hydrogen peroxide emulsion base and an alkaline (high pH) emulsion base.

The hydrogen peroxide emulsion base contains:

- 10 a) 35% by weight of an emulsion base premix comprising 10 % stearyl alcohol and 5% cetereth25;
b) 25% of an stabilizing solution comprising 1% tetrasodium DTPA, 0.4% HEDP, 1% sodium hydroxide (32% purity) and water q.s.p
c) 14% of water;
d) 26% of a solution of hydrogen peroxide (35% purity).

- 15 The alkaline emulsion base contains:

- a) 0.2% by weight of sodium sulphite;
b) 0.2% of ascorbic acid;
c) 3% of ammonium acetate;
d) 44.5% of the same emulsion base premix used for the hydrogen
20 peroxide emulsion base;
e) 11% of an ammonia solution (30% purity) to set the pH to approximately 10;
f) **the amount to be tested of chelant or mixtures of chelants** (for example 3.8% by weight of the alkaline emulsion base of EDDS,
25 equivalent to 1.9% EDDS "on head");
g) q.s. of water.

The pH of the mixture is buffered to 10 by the alkaline emulsion base.

2g of the bleaching composition per g of hair to be treated was applied on the hair switches and massaged in thoroughly. The hair switches were then
30 wrapped in a plastic film and put in an oven at 30°C. After 30mn, they were removed from the oven and from the wrapping film and rinsed for 1mn in water.

0.1g of shampoo per g. of hair was then added and milked for 30s before rinsing for 30s. (The combined concentration of calcium and magnesium ions (water hardness) of the water used during all experiments (except for the preparation of the compositions tested, wherein water was distilled or dionised) was carefully kept at 9 grains per gallon (153 ppm), with a molar ratio of $\text{Ca}^{2+}/\text{Mg}^{2+}$ equal to 3:1. The concentration of copper (Cu^{2+}) ions was kept at about 1 ppm (+/- 10%), the exact concentrations being measured by a standard analytic method. The rinsing water flow was adjusted to 6 liters per minute.) Then 0.1g of shampoo per g. of hair was added again and milked again for 30s before rinsing for another 30s. The excess water was then squeezed out of the hair, and the hair dried with a fan. Any standard shampoo can be used in this protocol as long as it is free from transition metal ions such as copper ion and that the level chelants is less than 0.1% by weight of the shampoo. Prell® shampoo was using during these tests.

This Oxidative Hair Treatment Protocol can be repeated several times. When damage is measured according to the FT-IR Damage Assessing Protocol (described below) the Oxidative Hair Treatment Protocol is preferably repeated 5 times and this process is described as a 5-Cycle Oxidative Hair Treatment Protocol.

FT-IR Damage Assessing Protocol

Damage caused to the hair was assessed by the FT-IR (Fourier Transform Infrared) method, which has been established to be suitable for studying the effects of oxidative treatments on hair (Strassburger, J., *J. Soc. Cosmet. Chem.*, **36**, 61-74 (1985); Joy, M. & Lewis, D.M., *Int. J. Cosmet. Sci.*, **13**, 249-261 (1991); Signori, V. & Lewis, D.M., *Int. J. Cosmet. Sci.*, **19**, 1-13 (1997)). In particular, these authors have shown that the method is suitable for quantifying the amount of cysteic acid that is produced from the oxidation of cystine. In general, the oxidation of cystine is thought to be a suitable marker by which to monitor the overall oxidation of the keratinous part of the fiber.

Net, the measurement of cysteic acid units by FT-IR is commonly used to study the effects of oxidative treatments or environmental oxidation upon keratin protein containing fibers such as hair and wool.

Signori & Lewis (D.M., *Int. J. Cosmet. Sci.*, **19**, 1-13 (1997)) have shown that FT-IR using a diamond Attenuated Total Internal Reflection (ATR) cell is a sensitive and reproducible way of measuring the cysteic acid content of single fibers and bundles. They have shown that this technique is more suitable than using the FT-IR method in simple transmission or microscope modes. They have also shown that the diamond cell ATR was significantly more sensitive and reproducible than the ZnSE cell. Hence, the method that we have employed to measure the cysteic acid content of multiple fiber bundles and full hair switches, is based upon the FTIR diamond cell ATR method employed by Signori and Lewis (1997). The detailed description of the method used for testing the different damage inhibitors follows thereafter:

A Perkin Elmer Spectrum® 1 Fourier Transform Infrared (FTIR) system equipped with a diamond Attenuated Total Internal Reflection (ATR) cell was used to measure the cysteic acid concentration in human hair. In this method, hair switches of various sizes and colours can be used. The switches were platted (~1 plait per cm) in order to minimize variations in surface area of contact between readings. The Oxidative Hair Treatment Protocol described above was repeated for 5 cycles to mimic the behavior of hair after repeated bleaching cycles. Following this treatment, four readings per switch were taken (~1/3 and 2/3s down the switch on both sides), and an average calculated. Backgrounds were collected every 4 readings, and an ATR cell pressure of 1N/m was employed. The cell was cleaned with ethanol between each reading, and a contamination check performed using the monitor ratio mode of the instrument. As prescribed by Signori & Lewis in 1997, a normalized double derivative analysis routine was used. The original spectra were initially converted to absorbance, before being normalized to the 1450cm^{-1} band (the characteristic and invariant protein CH_2 stretch). This normalized absorbance was then twice derivatised using a 13 point averaging. The value of the 1450cm^{-1} normalized 2nd

derivative of the absorbance at 1040cm^{-1} was taken as the relative concentration of cysteic acid. This figure was multiplied by -1×10^{-4} to recast it into suitable units. It was found that virgin human hair produced a value of ~ 20 cysteic acid units, and heavily oxidized hair produced values of >170 . The following

5 instrumental conditions were employed:

Spectral Resolution -	4cm^{-1}
Data Interval -	0.7cm^{-1}
Mirror Scan Speed -	0.2cms^{-1}
Number of Background Scans -	20
10 Number of Sample Scans -	20
Scan Range -	4000cm^{-1} to 600cm^{-1}

Using these instrumental conditions and the 2nd derivative analysis routine, it was found that the sensitivity and reproducibility of the method in the range 10 to 150 cysteic acid units, are both $\sim \pm 5-10\%$.

15

Comparative tests

The following illustrates the comparative effect of a typical embodiment of the present invention (EDDS) vs. 4 others chelants: ethylenediaminetetraacetic acid (EDTA), 1-hydroxyethane-1,1-diphosphonic acid (HEDP), diethylenetriaminepentaacetate (DTPA) and diethylenetriamine-N,N,N',N'',N''-penta(methylene phosphonate) (DTPMP). In this example, the molar

20 concentration of each of the 4 chelants was equal or greater to the concentration of EDDS ($0.053\text{ mol}/1000\text{g}$). Thus, it was possible to compare the effectiveness of each chelant vs., EDDS independent of their molecular weight. The corresponding weight percentage is indicated in the first line of the table below.

25

The tri-sodium salt of EDDS, tetra-sodium salt of EDTA, di-sodium salt of HEDP, penta-sodium salt of DTPA and tetra-sodium salt of DTPMP were used. EDTA and DTPA are commonly used in hair care compositions. HEDP was cited in US Patent No. 4,138,478 as useful for limiting the damage to the hair by nascent oxygen when included at a concentration of 0.1% by weight. DPTMP is

30 another phosphonate chelant.

In this experiment EDDS was tested at 1.9% by weight on head, but EDDS also provides excellent benefits at much lower concentrations. Damage and lightening effects were assessed after 5 cycles according to the test method described above ("Oxidative hair treatment protocol"). Human hair is often bleached or dyed 5 times or more during its life, which makes this 5 cycle test very meaningful. The results are shown in the table below:

Weight %	1.9% EDDS	2% EDTA	2.0% HEDP	2.65% DTPA	3.8 % DTPMP
Damage after 5 cycles (cysteic acid units)	110	165	163	147	142
Damage benefit vs EDTA 2%	+ 33 %	-	+ 1 %	+ 11 %	+14 %

Hair treated with 1.9% by weight EDDS displayed much less damage than hair treated with any other chelant. The value for damage without any added chelant is about 170 damaged cysteic units. The lightening effect of the oxidative composition was of about the same quality for all compositions.

EXAMPLES

The following examples illustrate oxidative dye compositions according to the present invention. It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to one skilled in the art without departing from the scope of the present invention.

Examples of formulation: emulsion

	1	2	3	4	5	6	7	8	9	10
Sodium sulphite	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Ascorbic Acid	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1

Ammonium Acetate	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Ammonia (30% active)	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Cetareth 25	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Cetyl Alcohol	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
Stearyl Alcohol	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3
Sodium Benzoate	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Phenoxyethanol	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
HBED (disodium salt of)	0.5	-	0.5	-	1.5	1.0	-	1.0	0.5	3.0
GADS (tetrasodium salt of)	-	0.5	0.5		-	-	0.5	-	0.5	-
EDDS (trisodium salt of)	-	1.0	-	0.6	0.5	1.0	0.5	-	0.5	-
Para-phenylene diamine	0.8	0.5	0.6	0.5	0.8	0.8	0.5	0.6	0.5	0.8
Para-aminophenol	0.2	0.3	0.2	0.1	0.2	0.2	0.3	0.2	0.1	0.2
Meta-aminophenol	1.0	0.5	1.0	0.6	1.0	1.0	0.5	1.0	0.6	1.0
Resorcinol	1.6	1.2	1.6	0.8	1.6	1.6	1.2	1.6	0.8	1.6
Hydrogen Peroxide (35% active)	8.6	8.6	8.6	13	17	17	17	34	34	34
Trimethylsilylamodi- methicone (SF1708)	0.5	0.5	1.5	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Polyquaternium 10 (Polymer JR30M)	0.2	0.2	--	0.2	0.2	0.2	0.2		-	-
Xanthan gum	0.5	0.5	-	1.0	0.5	0.5	0.5	0.5	0.5	1.0
Cetyl hydroxyethyl Cellulose (Natrosol 330CS Plus)	-	-	0.8	1.0	0.8	0.5	0.5	0.5	0.5	1.0
pH adjust to pH 10	qs	qs	qs	qs	qs	qs	qs	qs	qs	qs
Water	qs	qs	qs	qs	qs	qs	qs	qs	qs	qs

Example of formulation: thickened aqueous solution

1	2	3	4	5	6	7	8	9	10
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Sodium sulphite	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Ascorbic Acid	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Citric Acid	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Ammonia (30% active)	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Acrylates Copolymer (Aculyn® 33A)	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4
Oleth 10	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Oleth 2	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Oleic Acid	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9
Cocamide DEA	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
HBED (trisodium salt of)	0.5	-	0.5	-	1.5	1.0	-	1.0	0.5	3.0
GADS (tetrasodium salt of)	-	0.5	0.5		-	-	0.5	-	0.5	-
EDDS (trisodium salt of)	-	1.0	-	0.6	0.5	1.0	0.5	-	0.5	-
Para-phenylene diamine	0.8	0.5	0.6	0.5	0.8	0.8	0.5	0.6	0.5	0.8
Para-aminophenol	0.2	0.3	0.2	0.1	0.2	0.2	0.3	0.2	0.1	0.2
Meta-aminophenol	1.0	0.5	1.0	0.6	1.0	1.0	0.5	1.0	0.6	1.0
Resorcinol	1.6	1.2	1.6	0.8	1.6	1.6	1.2	1.6	0.8	1.6
Hydrogen Peroxide (35% active)	8.6	8.6	8.6	13	17	17	17	34	34	34
Behentrimonium Chloride	0.5	0.5	1.5	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Dicetyldimonium Chloride	0.2	0.2	0.7	0.2	0.2	0.2	0.2	-	-	-
Acrylates Steareth-20 Methacrylate Copolymer (Aculyn® 22)	0.5	0.5	-	1.0	0.5	0.5	0.5	0.5	0.5	1.0
Propylene Glycol	8.2	8.2	8.2	8.2	8.2	8.2	8.2	8.2	8.2	8.2
Ethoxy Diglycol	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2
pH adjust to pH 10	qs	qs	qs	qs	qs	qs	qs	qs	qs	qs

Water	qs qs qs qs qs qs qs qs qs qs
-------	--

The above compositions are useful for dyeing hair with reduced damage. Similar compositions not including oxidative dye precursors and couplers (in the above examples para-aminophenol, meta-aminophenol and resorcinol) can be used for bleaching (lightening) hair.

Oxidative hair dye compositions are usually sold in kits comprising, in separate containers, a dye component (also called "dye cream" for emulsion or "dye liquid" for solution) comprising the oxidative dye precursors (and usually the Hair Swelling Agent) and a hydrogen peroxide component (also called "hydrogen peroxide cream" for emulsion or "hydrogen peroxide liquid" for solution) comprising the oxidizing agent (usually hydrogen peroxide). The consumer mixes the dye component and hydrogen peroxide component immediately before use. The examples of the tables above illustrate the resulting mixtures.

Similarly, bleaching compositions are usually sold as a kit comprising two or three separate containers. The first contains the hair-swelling agent (e.g. ammonia), the second contains the oxidizing agent and the third (optional) contains a second oxidizing agent (e.g. alkali or ammonium salt of persulphates, percarbonate, perborate). The bleaching compositions are obtained by mixing the above-mentioned compositions immediately before use.

These kits are well known in the art and the composition in each container can be manufactured utilizing any one of the standard approaches, these include:

- Oil in water process
- Phase Inversion process
- One-pot process

The chelants are usually added to a proportion of the water at the start of the making process at ambient temperature, and allowed to dissolve. The fatty components are then added and the mixture is processed as is normal for the

above outlined procedures. For example, in a 1 pot process the polymers and chelants would be predissolved in water, the fatty materials added and then the whole heated to about 70-80°C.

5 A controlled cooling and optional shearing process to form the final structured product in the case of an emulsion would then follow. Addition of the ammonia and pH trimming complete the making process of the dye cream.

10 In the case of a liquid solution comprising acrylate polymers, these would be formulated into the hydrogen peroxide component. The glycol solvents and fatty components are formulated into the dye component. A structured product is formed when the dye and hydrogen peroxide components are mixed together prior to use of the composition, through deprotonation of the polymer acrylic acid groups yielding a polymeric micro-gel. Further details on the manufacture of these two-part aqueous composition for coloring hair, which forms a gel on mixing of the two parts can be found in US 5,376,146, Casperson et al. and
15 US5,393,305, Cohen et al.

The composition of the present invention can also be formulated as 2-part aqueous compositions comprising polyetherpolyurethane as thickening agent (such as Aculyn ® 46) as described in US 6,156,076, Casperson et al. and US6,106,578, Jones.

20 When the compositions of different containers are mixed before use and the resulting mixture comprises the chelants claimed, there is no preference on how the chelants are distributed in these containers. Obviously chelants that can be altered by hydrogen peroxide (or any oxidizing agent used) such as secondary amine chelants should however be formulated in the dye component.
25 The hydrogen peroxide component should however preferably comprise at least about 0.1% of a stable chelant to stabilize hydrogen peroxide. This stabilizer is required to prevent the hydrogen peroxide from decomposing too rapidly. For example EDTA can be used in the hydrogen peroxide component as stabilizer.

METHODS OF USE

30

Without pretr atment

The chelants according to the present invention are preferably formulated directly in the oxidizing compositions applied on hair (e.g. oxidative dye composition or bleach).

Oxidative dye

5 Oxidative dye compositions are usually sold as a kit comprising at least two separate containers: one contains the oxidative dye precursors with the hair-swelling agent (e.g. ammonia) in a suitable carrier (e.g. dye cream or liquid) and the other contains the oxidizing agent in a suitable carrier (e.g. hydrogen peroxide cream or liquid). The consumer prepares the oxidative dye composition
10 immediately before use by mixing both compositions and applies it on hair. After working the mixture a few minutes (to insure uniform application to all of the hair), the oxidative dye composition is allowed to remain on the hair for an amount sufficient for the dyeing to take place (usually about 30 minutes). The consumer then rinses his/her hair thoroughly with tap water and allows it to dry. It
15 is observed that the hair has changed from its original color to the desired color.

When present, the optional conditioning agent can be packaged partly or in totality in a third container. In this case, all three compositions can be mixed immediately before use and applied together, or the content of the third container can be applied (after an optional rinse step) as a post-treatment immediately
20 after the oxidative dye composition resulting from the mixture of the other containers.

Bleaching compositions

Bleaching compositions are usually sold as a kit comprising two or three separate containers. The first contains the hair-swelling agent (e.g. ammonia),
25 the second contains the oxidizing agent and the third (optional) contains a second oxidizing agent (e.g. alkali or ammonium salt of persulphates, percarbonate, perborate). The consumer prepares the bleaching compositions immediately before use by mixing all compositions and applies the mixture on hair (as for the oxidative dye composition) for an amount of time sufficient for the
30 bleaching to take place (usually about 30mn).

The optional conditioning agent can also be packaged partly or in totality in an additional third or fourth container. In this case, all compositions can be mixed together immediately before use or the content of the additional container can be applied (with an optional preliminary rinse step) as a post-treatment immediately after the bleaching composition resulting from the mixture of the other containers.

With pretreatment

The chelants can also be applied to hair as a pre-treatment. The pretreatment composition ("first composition") can be applied immediately before the oxidizing composition ("second composition") or after a longer period of time.

Pretreatment immediately followed by an oxidizing composition

In the case of a pretreatment applied on hair and immediately followed by the oxidizing composition, said pretreatment composition can be rinsed off hair before the application of the oxidizing composition, but will be preferably kept on the hair during the application of the oxidizing compositions, the resulting mixture being rinsed off following the oxidizing step. Kits comprising one container for the first composition (pre-treat) and one, two or more containers for the second composition (oxidizing composition) can be advantageously used for this method. Two containers or more can be required for the second composition in case this second composition is prepared immediately before use by mixing the content of two containers or more (e.g. oxidative hair dye composition or bleaching composition). The kit can also comprise an additional container for a composition comprising a conditioning agent that is applied independently from the second composition in a third step, optionally following a rinsing step.

Color care

The pretreatment can also take place as a "color care" treatment anytime between two oxidative treatments but not immediately prior to one. The 2 oxidative treatments are preferably separated by at least one day, more preferably at least one week. Oxidative hair dye treatments are generally

repeated about once a month and obviously, hair will be usually rinsed with water immediately after each oxidative treatment. The "color care" treatment can be repeated as many times as practical between the two oxidative treatments, which can be once, twice or more.

WHAT IS CLAIMED IS:

1. A composition suitable for treating hair comprising:

a) an oxidizing agent; and

b) a chelant (L) having a $\frac{\log K_{CuL}}{\log K_{CaL}}$ ratio calculated at pH 10 of at least

5 3.20, preferably at least 3.30, more preferably at least 3.40, even more preferably at least 3.50;

wherein $\log K_{CuL}$ is the common logarithm of the Conditional Stability Constant of said chelant with Cu^{2+} and $\log K_{CaL}$ is the common logarithm of the Conditional Stability Constant of said chelant with Ca^{2+} .

10

2. A composition according to claim 1, wherein said chelant has a Hydrogen Peroxide Decomposition Ratio (% Loss) of less than 3.5%, preferably less than 2.5%, even more preferably less than 2% as measured by the Hydrogen Peroxide Decomposition Ratio Measurement Protocol described
- 15 herein and/or said chelant forms a hexadendate complex with Cu^{2+} .

3. A composition suitable for treating hair comprising:

a) an oxidizing agent; and

20 b) a chelant selected from the group consisting of diamine-N,N'-dipolyacids, monoamine monoamide-N,N'-dipolyacids and N,N'-bis(2-hydroxybenzyl)ethylenediamine-N,N'-diacetic acid (HBED), derivatives thereof, salts thereof and mixtures thereof.

4. A composition according to Claim 3, wherein said polyacids contain at least
- 25 two acid groups independently selected from the carboxylic acid group (-COOH), sulphonic group (-SO₃H), the o-hydroxyphenyl group, the m-hydroxyphenyl group and the p-hydroxyphenyl group.

5. A composition according to Claim 4, wherein said chelant is selected from the group consisting of ethylenediamine-N,N'-disuccinic acid (EDDS), ethylenediamine-N,N'-diglutamic acid (EDDG), 2-hydroxypropylenediamine-N,N'-disuccinic acid (HPDDS), glycine-N,N'-disuccinic acid (GADS),
5 ethylenediamine-N,N'-bis(ortho-hydroxyphenyl acetic acid) (EDDHA), salts thereof, derivatives thereof, and mixtures thereof.
6. A composition according to Claim 5, wherein said chelant is selected from ethylenediamine-N,N'-disuccinic acid, salts thereof, derivatives thereof and
10 mixtures thereof.
7. A composition according to any of the preceding Claims, wherein the pH of the composition is above 8, preferably between 8 and 12, more preferably between 9 and 11.5, even more preferably between 9.5 and 11.
15
8. A composition according to any of the preceding Claims, wherein said composition is in the form of an oil-in-water emulsion or a thickened aqueous solution.
- 20 9. A composition according to any of the preceding Claims, wherein said oxidizing agent is present at a level of from 0.1% to 40% by weight of said composition and is selected from water-soluble oxidizing agents and mixtures thereof, preferably hydrogen peroxide.
- 25 10. A composition according to any of the preceding Claims, wherein said chelant is present at a level of from 0.01 to 10%, preferably from 0.1 to 5%, more preferably from 0.5 to 2% by weight of said composition.
- 30 11. A composition according to any of the preceding Claims, further comprising at least one oxidative hair dye precursor.

12. A method of treating hair comprising the step of contacting hair with a composition according to any of the preceding Claims.
13. A method of treating hair comprising the subsequent steps of:
- 5 i) contacting hair with a first composition comprising a chelant (L) having a $\frac{\log K_{CuL}}{\log K_{CaL}}$ ratio calculated at pH 10 of at least 3.20, preferably at least 3.30, more preferably at least 3.40, even more preferably at least 3.50;
- ii) contacting hair with a second composition comprising an oxidizing agent immediately after step i);
- 10 wherein $\log K_{CuL}$ is the common logarithm of the Conditional Stability Constant of said chelant with Cu^{2+} and $\log K_{CaL}$ is the common logarithm of the Conditional Stability Constant of said chelant with Ca^{2+} .
14. A method of treating hair comprising the subsequent steps of:
- 15 i) contacting hair with a first composition comprising an oxidizing agent;
- ii) contacting hair with a second composition comprising a chelant having a $\frac{\log K_{CuL}}{\log K_{CaL}}$ ratio calculated at pH 10 of at least 3.20, preferably at least 3.30, more preferably at least 3.40, even more preferably at least 3.50; and
- 20 iii) contacting hair with a third composition comprising an oxidizing agent;
- wherein steps i) and iii) are separated by at least 1 day and step ii) does not take place immediately before step iii); and
- wherein $\log K_{CuL}$ is the common logarithm of the Conditional Stability Constant of said chelant with Cu^{2+} and $\log K_{CaL}$ is the common logarithm of the Conditional Stability Constant of said chelant with Ca^{2+} .
- 25
15. A kit for dyeing hair comprising a first and a second compositions packaged in different containers, wherein said first composition comprises an oxidizing agent and said second composition comprises an oxidative dye

precursor, characterized in that the resulting mixture of said first and second compositions is a composition according to Claim 11.

16. A method of dyeing human hair comprising the subsequent steps of:

- 5 i) mixing the first and second composition of a kit according to Claim 15;
- ii) contacting hair with the mixture obtained on step i);
- iii) massaging said mixture into hair;
- iv) retaining said mixture on the hair for an amount of time sufficient for mixture to dye the hair;
- 10 iv) rinsing off said composition with water.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 02/08477

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61K7/135

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A61K C11D D06L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	WO 97 24106 A (DIAS LOUIS CARLOS ;PULLAN ROWENA JULIET FLUX (GB); SANGER ALISON J) 10 July 1997 (1997-07-10) cited in the application page 36, paragraph 2 -page 37, paragraph 4 page 18, last paragraph claims 1,19,20; examples 1-6	3-12,15, 16
A	US 6 024 891 A (HUGHES IAIN ALLAN) 15 February 2000 (2000-02-15) column 10, line 31 - line 51; claim 1 column 1, paragraph 2	3-6,10
A	EP 1 001 011 A (PROCTER & GAMBLE) 17 May 2000 (2000-05-17) paragraphs '0133!,'0135!; claims 1,2,7-11; examples	3-9

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents.

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *8* document member of the same patent family

Date of the actual completion of the international search

19 July 2002

Date of mailing of the international search report

31/07/2002

Name and mailing address of the ISA

European Patent Office, P.B 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Angiolini, D

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1 2

Present claims 1,2,7-16 (as far as they refer back to cls.1,2) relate to a composition defined (inter alia) by reference to the following parameters:

P1: $\log K_{CuL}/\log K_{CaL}$

P2: Hydrogen Peroxide Decomposition Ratio

The use of these parameters in the present context is considered to lead to a lack of clarity within the meaning of Article 6 PCT. It is impossible to compare the parameters the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaningful complete search impossible. Consequently, the search has been restricted to the parts relating to the composition as described in cls.3-6.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

national application No.
PCT/US 02/08477

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1 2
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 02/08477

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9724106	A	10-07-1997	BR 9612328 A	02-03-1999
			BR 9612384 A	13-07-1999
			CN 1209055 A	24-02-1999
			CN 1209054 A	24-02-1999
			EP 0869769 A1	14-10-1998
			EP 0879045 A1	25-11-1998
			JP 2002509519 T	26-03-2002
			WO 9724108 A1	10-07-1997
			WO 9724106 A1	10-07-1997
US 6024891	A	15-02-2000	AU 711063 B2	07-10-1999
			AU 4415396 A	10-07-1996
			BR 9510455 A	26-05-1998
			CA 2208462 A1	27-06-1996
			CN 1170431 A	14-01-1998
			CZ 9701885 A3	12-11-1997
			EP 0799300 A1	08-10-1997
			HU 77291 A2	30-03-1998
			JP 10510874 T	20-10-1998
			KR 239803 B1	01-07-2000
			NZ 298623 A	25-02-1999
			PL 320867 A1	10-11-1997
			SK 82997 A3	14-01-1998
			TR 960612 A2	21-07-1996
			WO 9619562 A1	27-06-1996
EP 1001011	A	17-05-2000	EP 1001010 A1	17-05-2000
			EP 1001011 A2	17-05-2000
			AU 1816800 A	29-05-2000
			TR 200101308 T2	22-10-2001
			WO 0027972 A1	18-05-2000
			AU 1816500 A	29-05-2000
			WO 0027978 A1	18-05-2000

